

OGOSH49USA

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:)	
)	Examiner:
Yuichiro Shindo et al.)	
)	Group Art Unit:
Application No.:)	
)	
Corresponding International Filing No.:)	
PCT/JP2004/013031)	
)	
Filed: Herewith)	
)	
For: HIGH PURITY ZINC OXIDE)	
POWDER AND METHOD FOR)	
PRODUCTION THEREOF, AND)	
HIGH PURITY ZINC OXIDE)	
TARGET AND THIN FILM OF)	
HIGH PURITY ZINC OXIDE)	

Mail Stop PCT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

VERIFICATION OF TRANSLATION

Sir:

I, Isamu Ogoshi, having been warned that willful false statements and the like are punishable by fine or imprisonment or both, under section 1001 of Title 18 of the United States Code, and may jeopardize the validity of the above-captioned application and any patent issuing thereon, declare:

(1) I am a patent attorney authorized to practice law in Japan and am engaged in the practice of law with OGOSHI International Patent Office at Toranomom 9 Mori Bldg. 3F, 2-2, Atago 1-Chome, Minato-ku, Tokyo 105-0002, Japan.

(2) I am fluent in the Japanese and English Languages.

(3) I have reviewed the attached translation, and certify that it is an accurate English translation of the Japanese language international application of Yuichiro Shindo and Kouichi Takemoto filed on September 8, 2004 and given International Application No. PCT/JP2004/013031.

(4) All of the statements made herein of my own knowledge are true and all statements made herein on information and belief are believed to be true.

March 6, 2006

Date

Isamu Ogoshi

Isamu Ogoshi

Customer No.: 00270

Attorney Docket No.: OGOSH49USA

HIGH PURITY ZINC OXIDE POWDER AND METHOD
FOR PRODUCTION THEREOF, AND HIGH PURITY ZINC OXIDE
TARGET AND THIN FILM OF HIGH PURITY ZINC OXIDE

TECHNICAL FIELD

The present invention pertains to high purity zinc oxide powder and the
10 manufacturing method thereof, a sputtering target obtained by firing this high
purity zinc oxide powder, and a high purity zinc oxide thin film formed by
sputtering this target.

BACKGROUND ART

15

Zinc oxide (ZnO) is white-colored powder, also known as zinc flower or
zinc white, and is powder having hexagonal crystals.

Zinc oxide is used as white pigment for paint and artists' colors, and is
also used as pharmaceuticals or cosmetics. Further, in recent years, zinc
20 oxide is being used as a sputtering target material for forming thin films to be
used in electronic components such as a semiconductor device.

Commercially available zinc oxide has a purity level of 95 to 99.9wt%,
and it is necessary to purify this further to obtain a purity level of 4N to 5N.
In particular, C, Cl and S must be sufficiently reduced since these
25 respectively form carbide, chloride and sulfide together with Zn.

As conventional technology, there is a method of collecting Zn from Zn-
containing dust, and, with this method, Zn-containing dust containing Fe and
Pb is leached with sulfuric acid solution, and subject to solvent extraction

with D2EHPA. With this technology, although there is an effect in the removal of Fe, there is a problem in that Pb, Si and Al cannot be sufficiently removed (e.g., refer to Patent Documents 1 and 2).

Further disclosed is a wet generation method of zinc oxide for directly
5 generating zinc oxide in a solution by neutralizing an aqueous solution containing zinc salt in antalkali (refer to Patent Document 3). Nevertheless, there is no particular description regarding the removal of C, Cl, S and Pb, and it is also speculated that this is accepting the existence of C, Cl, S and Pb.

10 Meanwhile, since high purity zinc having a purity level of 6N exists, it is also possible to consider oxidizing this to obtain high purity zinc oxide. Nevertheless, since this will become extremely costly, it is not realistic for industrial manufacture.

15 [Patent Document 1]

Japanese Patent Laid-Open Publication No. S59-116339

[Patent Document 2]

Japanese Patent Laid-Open Publication No. S59-126729

[Patent Document 3]

20 Japanese Patent Laid-Open Publication No. S53-116296

DISCLOSURE OF THE INVENTION

Thus, an object of the present invention is to provide high purity zinc
25 oxide and the manufacturing method thereof in which impurities, in particular C, Cl, S and Pb impurities, can be efficiently removed at low cost by subjecting Zn-containing raw material to acid leaching or electrolytic extraction, and thereafter subject this to solvent extraction and activated

carbon treatment. Another object of the present invention is to provide a target obtained by firing this high purity zinc oxide, and a high purity zinc oxide thin film obtained by sputtering this target.

The present invention provides:

- 5 1. High purity zinc oxide powder, high purity zinc oxide sputtering target and high purity zinc oxide thin film wherein the impurity content excluding gas components of N, C, Cl, S and P is less than 100wtppm;
2. High purity zinc oxide powder, high purity zinc oxide sputtering target and high purity zinc oxide thin film wherein the impurity content excluding gas
10 components of N, C, Cl, S and P is less than 10wtppm;
3. High purity zinc oxide powder, high purity zinc oxide sputtering target and high purity zinc oxide thin film according to paragraph 1 or paragraph 2 above, wherein the total content of gas components of C, Cl and S is less than 100wtppm;
- 15 4. High purity zinc oxide powder, high purity zinc oxide sputtering target and high purity zinc oxide thin film according to any one paragraphs 1 to 3 above, wherein the Pb content as impurities is less than 5wtppm;
5. High purity zinc oxide powder, high purity zinc oxide sputtering target and high purity zinc oxide thin film according to any one paragraphs 1 to 4
20 above, wherein Mg and Al are respectively less than 1wtppm;
6. High purity zinc oxide sputtering target and high purity zinc oxide thin film according to any one paragraphs 1 to 5 above, wherein the crystal grain size of zinc oxide is 100 μ m or less;
7. A manufacturing method of high purity zinc oxide powder including the
25 steps of subjecting a raw material such as Zn-containing scrap to acid leaching or electrolytic extraction, thereafter performing solvent extraction and activated carbon treatment thereto in order to remove impurities, neutralizing the resultant solution freed of impurities with an alkaline solution

to obtain zinc hydroxide, and firing the zinc hydroxide to obtain zinc oxide;

8. The manufacturing method of high purity zinc oxide powder according to any one of paragraphs 1 to 5 above, including the steps of subjecting a raw material such as Zn-containing scrap to acid leaching or electrolytic extraction, thereafter performing solvent extraction and activated carbon treatment thereto in order to remove impurities, neutralizing the resultant solution freed of impurities with an alkaline solution to obtain zinc hydroxide, and firing the zinc hydroxide to obtain zinc oxide; and

9. The manufacturing method of high purity zinc oxide powder according to paragraph 7 or paragraph 8 above, wherein the grain size of zinc oxide powder is 0.1 to 100 μ m.

[Effect of the Invention]

The present invention yields a superior effect in that high purity zinc oxide can be manufactured at low cost by dissolving a zinc-containing raw material having a purity level of 90 to 99.9wt% with acid, and thereafter subjecting this to solvent extraction and activated carbon treatment in order to effectively remove impurities.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flowchart showing the manufacturing method of high purity zinc oxide.

BEST MODE FOR CARRYING OUT THE INVENTION

Examples of analytical values of the zinc-containing raw material are shown in Table 1. As shown in Table 1, this raw material contains Pb and

Fe at 100wtppm or more; Cu, Cd, Th, Mg, Na, B and Li at roughly 10 to 80wtppm; impurities such as Ni, Co, Sn, Sb, W, Mo, Ga and Co respectively at roughly 1 to 10wtppm; and gas components of N, C, Cl, S and P at roughly 50wtppm to 3wt%.

5

10

15

20

25

Table 1

wtppm

Impurities	Raw material	Example 1	Example 2	Example 3
P b	1 0 0	<0.1	0.2	0.5
F e	1 1 5	<0.1	<0.1	0.3
C r	8	<0.1	<0.1	0.1
N i	6	<0.1	<0.1	<0.1
C u	1 0	<0.1	<0.1	<0.1
A l	5	0.3	<0.1	<0.1
C d	2 0	0.2	<0.1	<0.1
S n	5	0.3	<0.1	<0.1
S b	1	<0.1	<0.1	<0.1
W	1	<0.1	<0.1	<0.1
T l	3 5	0.1	0.2	0.7
M o	2	<0.1	<0.1	<0.1
G a	1	<0.1	<0.1	<0.1
C o	3	<0.1	<0.1	<0.1
M n	1	<0.1	<0.1	<0.1
T i	4	<0.1	0.3	<0.1
K	5	<0.1	0.3	<0.1
M g	1 3	<0.1	0.2	<0.1
N a	8 0	<0.1	0.2	<0.1
B	1 0	<0.1	0.2	<0.1
L i	5 0	<0.1	0.2	<0.1
N	2 0 0 0	100	70	300
C	1 %	50	80	30
C l	5 0 0	3	10	30
S	3 %	8	20	50
P	5 0	<0.1	<0.1	<0.1
Number of Particles		5	7	1 0

As described above, in particular, as a sputtering target or thin film to be used in electronic components such as a semiconductor device, high purity zinc oxide powder having a purity of 99.99wt% or more is required. In particular, it is necessary to reduce impurities excluding gas components of N, C, Cl, S and P to be less than 100wtppm since such impurities will have an adverse effect on the characteristics of ZnO. Preferably, the amount of impurities is less than 10wtppm.

Gas components of C, Cl and S must be sufficiently reduced since these respectively form carbide, chloride and sulfide. It is desirable that these are less than 100wtppm. Among the above, in particular, it is desirable that Cl is reduced as much as possible since it increases the leakage current when the TFT is turned off.

It is desirable that S is reduced as much as possible since it deteriorates the mobility due to the scattering of impurities. Further, C, Cl and S all cause the increase of particles during sputtering.

Further, it is desirable that the Pb content is less than 5wtppm since Pb deteriorates the electrical mobility due to the scattering of impurities and has an adverse effect on ZnO. It is desirable that the Mg content and Al content are respectively less than 1wtppm since Mg and Al have stronger oxidizing power than Zn, deprive oxygen from ZnO, create oxygen loss, and further increase the leakage current when the TFT is turned off.

Upon manufacturing high purity zinc oxide powder, zinc-containing raw material is dissolved with acid at room temperature, and thereafter subject to solvent extraction and activated carbon treatment in order to remove impurities such as organic matter and foreign matter and impurities such as Pb described above. As the solvent, D2EHPA (D2 ethylhexyl phosphoric acid) may be used.

Upon performing acid dissolution, any acid capable of dissolving zinc

may be used. As an example, acid leaching may be performed with nitric acid. Or zinc may be dissolved via electrolysis.

Thereafter, the resultant solution is neutralized with alkaline solution to obtain high purity zinc hydroxide ($\text{Zn}(\text{OH})_2$). As the alkaline solution, in particular, it is desirable to use ammonium hydroxide. The use of sodium hydroxide or potassium hydroxide is undesirable since high concentrations of Na and K will be respectively mixed in the zinc oxide.

The zinc hydroxide obtained as described above is fired at 100 to 500°C in order to obtain zinc oxide (ZnO) powder of 0.1 to 100 μm . As a result of the foregoing processing steps, it is possible to reduce various impurities, excluding gas components, to be 1ppm or less or 0.1ppm or less, and obtain high purity zinc oxide having a purity level of 5N or more. The flow of the manufacturing method of high purity zinc oxide according to the present invention is shown in FIG. 1.

This zinc oxide powder is further hot pressed and formed into a sputtering target. As an example of the hot pressing conditions, this may be performed under oxygen atmosphere at, for instance, 1200°C \times 5hr.

This target is further sputtered under oxygen atmosphere to obtain a high purity zinc oxide thin film.

[Examples]

Examples of the present invention are now explained. These Examples are merely illustrative, and the present invention shall in no way be limited thereby. In other words, the present invention shall only be limited by the scope of the present invention, and shall include the various modifications other than the Examples of this invention.

(Example 1)

100g of raw material having a zinc content level of 90wt% and containing the impurities shown in Table 1 was subject to acid leaching with

1L of acid containing 10% nitric acid to obtain a solution having a zinc concentration of 90g/L.

Next, the resultant solution was subject to solvent extraction with D2EHPA. This was further subject to activated carbon treatment in order to remove impurities such as organic matter and Pb. Thereafter, this was neutralized with NH_4OH to obtain high purity zinc hydroxide ($\text{Zn}(\text{OH})_2$).

The obtained high purity zinc hydroxide was fired at 200°C to obtain high purity zinc oxide (ZnO) powder having an average grain size of $10\mu\text{m}$. The analysis of impurities of the high purity zinc oxide is shown in Table 1.

As shown in Table 1, the various impurities listed in Table 1, excluding gas components, were respectively reduced to 1wtppm or less or 0.1wtppm or less, and high purity zinc oxide powder having a purity level of 5N or more was obtained thereby. A significant improvement in purity was confirmed based on the processing steps shown in Example 1 of the present invention.

This high purity zinc oxide powder was used to manufacture a sputtering target by further performing hot pressing and sintering at 1200°C for 5hr under the flow volume of 5ml/min of oxygen gas. This target was sputtered under oxygen atmosphere, and, in comparison to conventional targets, it was possible to form a high purity zinc oxide thin film on the substrate. As the level of particles on the thin film, there were 5 particles of $0.2\mu\text{m}$ or larger.

The various impurities contained in the raw material are particularly disfavored in the manufacture of semiconductor devices and the like, and the reduction of these impurities is extremely effective.

(Example 2)

The same raw material as Example 1 was used, and electrolysis was performed with pH2 ammonium nitrate solution in order to extract Zn in the solution. Impurities were removed with the same method as Example 1.

The impurities analysis and the like are similarly shown in Table 1.

(Example 3)

The same raw material as Example 1 was used, and electrolysis was performed with pH2 ammonium nitrate solution again in order to extract Zn in the solution. Impurities were removed with the same method as Example 1. The impurities analysis and the like are similarly shown in Table 1.

(Comparative Example 1)

100g of raw material having a zinc content level of 90wt% and containing the impurities as with Example 1 was subject to acid leaching with 1L of acid containing 10% hydrochloric acid and 10% hydrogen peroxide to obtain a solution having a zinc concentration of 90g/L.

NH₄OH was added to this resultant solution and neutralized to pH8 in order to obtain zinc hydroxide (Zn(OH)₂).

This was further fired at 200°C to obtain zinc oxide (ZnO) powder. The analysis of impurities of the obtained zinc oxide is shown in Table 2.

As shown in Table 2, most of the various impurities shown in Table 1 were hardly reduced.

Table 2

w t p p m

Impurities	Raw material	Comparative Example 1	Comparative Example 2	Comparative Example 3
P b	1 0 0	8 0	2 0	<0.1
F e	1 1 5	7 4	<0.1	<0.1
C r	8	2	1 . 7	<0.1
N i	6	5	4	<0.1
C u	1 0	2	1	<0.1
A l	5	4	1	0 . 3
C d	2 0	1 5	4	0 . 2
S n	5	1	1	0 . 3
S b	1	<1	<1	<0.1
W	1	<1	<1	<0.1
T l	3 5	2 0	1 2	0 . 1
M o	2	1	<1	<0.1
G a	1	<1	<1	<0.1
C o	3	1	<1	<0.1
M n	1	<1	<1	<0.1
T i	4	2	<1	<0.1
K	5	3	2	0 . 5
M g	1 3	1 0	7	<0.1
N a	8 0	7 0	4 0	1 5 0
B	1 0	4	1	<0.1
L i	5 0	4 0	1 5	<0.1
N	2 0 0 0	8 5 0	1 %	1 0 0
C	1 %	7 0 0	5 %	5 0
C l	5 0 0	4 0 0	1 0 0	3
S	3 %	1 %	2 0 0	8
P	5 0	1	5 0	<0.1
Number of Particles		700	1000	250

(Comparative Example 2)

100g of raw material having a zinc content level of 90wt% and containing the impurities as with Example 1 was subject to acid leaching with 1L of acid containing 10% hydrochloric acid and 10% hydrogen peroxide to
5 obtain a solution having a zinc concentration of 90g/L.

Next, the resultant solution was subject to solvent extraction with D2EHPA to remove impurities. Incidentally, the activated carbon treatment shown in Example 1 was not performed. NH_4OH was added to this resultant solution and neutralized to pH8 in order to obtain zinc hydroxide
10 $(\text{Zn}(\text{OH})_2)$.

This was further fired at 200°C to obtain zinc oxide (ZnO) powder. The analysis of impurities of the obtained zinc oxide is shown in Table 2.

As shown in Table 2, although the purity improved in comparison to Comparative Example 1, impurities such as Pb, Tl, Na, Li, Na, Cl, S and P
15 were contained in a considerable amount, and the effect of sufficiently removing impurities could not be realized. Therefore, it is evident that activated carbon treatment is important when compared with Example 1.

(Comparative Example 3)

100g of raw material having a zinc content level of 90wt% and
20 containing the impurities as with Example 1 was subject to acid leaching with 1L of acid containing 10% hydrochloric acid and 10% hydrogen peroxide to obtain a solution having a zinc concentration of 90g/L.

Next, the resultant solution was subject to solvent extraction with D2EHPA. This was further subject to activated carbon treatment to remove
25 impurities such as organic matter and Pb. Thereafter, this resultant solution was neutralized with NaOH in order to obtain high purity zinc hydroxide $(\text{Zn}(\text{OH})_2)$.

This was further fired at 200°C to obtain high purity zinc oxide (ZnO)

powder. The analysis of impurities of the obtained high purity zinc oxide is shown in Table 2.

As shown in Table 2, zinc oxide in which impurities excluding Na and K equal to Example 1 was obtained. In particular, the increase of Na is due to
5 the neutralization with NaOH, and it is evident that the use of ammonia water as the neutralizing agent is important.

[Industrial Applicability]

The present invention yields a superior effect in that high purity zinc oxide can be manufactured at low cost by dissolving a commercially available
10 zinc-containing raw material having a purity level of 90wt% with acid, and thereafter subjecting this to solvent extraction and activated carbon treatment in order to effectively remove impurities, and is extremely useful as a target material for electronic components such as a semiconductor device.